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PREPARATION AND EVALUATION OF ADVANCED ELECTROCATALYSTS FOR
PHOSPHORIC ACID FUEL CELLS

6TH QUARTERLY REPORT

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ABSTRACT

The previous Quarterly Report concentrated on electrocatalysts for anodic fuel cell reactions (oxidation of hydrogen in the presence of carbon monoxide). This Quarterly Report concentrates on the performances of electrocatalysts of binary element electrocatalysts for oxygen molecule reduction in hot phosphoric acid.

Electrocatalysts formed from platinum combined with transition metal carbide forming elements (W, Mo, V) have been constructed and preliminary steps were taken to characterize their surface elemental distributions and particle sizes. Utilizing the most recent advances for carbon supports (Consel IV) developed in our parallel EPRI 1200-2 program, the highest performance electrocatalyst combination ever observed gives 755 mV vs hydrogen at 100 ASF on air at 180°C and shows a potential improvement to 775 mV vs hydrogen for better electrode structures. A pressurized fuel cell (UTC at 5 atm) would then give 805 mV at 320 ASF and 180°C. Another activity diagnostic is the performance of this electrocatalyst on oxygen at 900 mV vs hydrogen. The value for our electrocatalyst is 44 mA per milligram of platinum and is projected to reach 60 mA per milligram of platinum with improved electrode structures. Since the electrocatalyst surface area has not been optimized and the electrode structure has not been optimized, there is considerable room for performance enhancement beyond these values, especially at higher temperatures.

There are now significant economic possibilities to either operate fuel cells at higher current densities or for halving the noble metal loading at fuel cell cathodes.

1. Objective and Scope of Work

The overall objective of this electrocatalysis program is to define the feasibility of lowering the electrocatalyst cost and to increase the activity in phosphoric acid fuel cells, as a way to increase the commercial viability of fuel cells for producing electric power.

The specific objectives of the present tasks are the preparation of a series of high surface area electrocatalysts for evaluation in phosphoric acid fuel cells. This involves fabrication of efficient gas-diffusion electrode structures and determining their electrochemical parameters for hydrogen oxidation and oxygen reduction. When possible, new experimental techniques and theoretical interpretations will be forwarded towards an understanding of the relevant electrochemical parameters.

2. Summary of Previous Work

Previously, materials developments under this contract have identified a number of binary alloy combinations as anode electrocatalysts for operation in hot phosphoric acid fuel cells. Due to the filing of patent applications on these materials by DOE, specific details of the alloy combinations are not given in this report. Suffice to say, anode electrocatalysts have been produced that perform as well as platinum supported on carbon but with a decrease in the electrocatalyst cost 50 to 80% from the same platinum catalyst/performance benchmarks previously discovered.

The catalysts have been tested on realistic fuel-gas mixtures containing 2 to 30% carbon monoxide. No performances have been determined with hydrogen sulphide as an electrocatalyst poison.

A unique feature for these new alloy catalyst formulations has been the reliance of the metal electrocatalyst particles on the structure of the carbon supports. New carbon supports having outstanding corrosion resistance when used for cathode electrocatalysts have shown that when applied as anode electrocatalyst supports, they confer stability on the electrocatalyst alloy particles. The reason for this stability has not been determined but is thought to be due to the matching of atomic structures between the carbon supports and the metal electrocatalyst particles. The carbon support development has been funded in a parallel program by the Electric Power Research Institute.

3. Technical Progress

3.4. Task 4 - Literature Survey and Selection

The relative rates of the gas phase H_2-D_2 equilibration reaction on the transition metals Pt, Rh, Ni, Fe, W, Mo, and Cr are remarkably similar (Stonehart and Ross, Cat. Revs., 12, 1, 1975). When operating in the presence of an acid electrolyte, however, the less noble of these elements, i.e. Ni, Fe, W, Mo, and Cr, perform poorly as hydrogen dissociation catalysts. Examinations of electrochemical equilibria data indicate that the surfaces of these elements are more characteristic of the oxides as opposed to the metals at hydrogen potentials. It is known that metal oxides are poorer hydrogen dissociation catalysts relative to the parent metal (Bond, Catalysis by Metals, Academic Press, 1962 and Clark, Ind. Eng. Chem., 45, 1476, 1953) so these materials are not expected to be promising candidates for anode electrocatalyst structures. Nevertheless, the transition metals should not be rejected out of hand. Some transition metal carbides, e.g. WC and Mo_2C , exhibit almost metallic activity

as hydrogen electrodes. It has been postulated that the effect of carbon is to stabilize the transition metal against oxidation (Ross and Stonehart, J. Cat., 48, 42, 1977). Furthermore, WC has the same electronic structure as platinum and exhibits many of the same catalytic properties (McNicol, Catalysis, V. 2, 243, 1978).

Platinum-molybdenum and platinum-tungsten alloys have been investigated for the electrochemical oxidation of methanol in acid electrolyte (Janssen and Moolhuysen, Electrochimica Acta, 21, 869, 1976). The Pt-Mo electrocatalyst exhibited activity 2-3 times that of platinum while the Pt-W electrocatalyst exhibited activity comparable to platinum. More importantly, the voltammetry for both alloys showed extended hydrogen adsorption peaks compared to platinum, and the hydrogen adsorption was stable. Hobbs and Tseung previously investigated hydrogen oxidation in acid electrolyte for Pt supported on WO_3 . A maximum in specific electrocatalytic activity was reported in the range 0.02 to 0.1 mg Pt/cm² (Hobbs and Tseung, J. Electrochem. Soc., 120, 766, 1973).

There is already extant evidence that molybdenum and tungsten in combination with platinum can be used at both the anode and cathode in phosphoric acid fuel cells. Platinum sodium tungsten bronzes (Niedrach and Zeliger, J. Electrochem. Soc., 116, 152, 1969), platinum molybdenum oxide, and platinum tungsten oxide (Niedrach and Weinstock, J. Electrochem. Soc., 3, 270, 1965) all show increased activity for $H_2 + CO$ oxidation. McKee and Pak have also reported increased activity for $H_2 + CO$ mixtures in phosphoric acid (McKee and Pak, J. Electrochem. Soc., 116, 516, 1969).

Since both tungsten and molybdenum do not chemisorb carbon monoxide to any appreciable extent (Ford, Adv. Cat., 31, 51, 1970), the ability of these electrodes to operate better than platinum is not surprising. Platinum is severely poisoned at the low temperatures used in the aforementioned research efforts. It is not clear whether this performance will hold up under current fuel cell operating temperatures (180-200°C). It was previously shown in this contract (Quarterly Report #5) that rhenium in combination with platinum did not perform as well as was expected as an anode. Rhenium is a member of the same family as tungsten and molybdenum and exhibits similar CO adsorption properties. Both tungsten and molybdenum are better carbide forming materials, however, so they should not be prejudged on the basis of the rhenium formulations.

The molybdenum-platinum and tungsten-platinum alloys are also promising cathode materials. WC and $MoSi_2$ have been used as cathodes on air and oxygen (Thompson and Heath, U.S. 3,346,421, 1967). Of particular interest is the ability of

molybdenum to stabilize supported platinum. Pt surface area retention has been demonstrated for the Mo^{2+} ion (Eimakov, et al., Kinet. Katal., 15, 1093, 1974). In addition to surface area retention, improved Pt activity has been reported for addition of MoO_3 to $\text{Pt/Al}_2\text{O}_3$ catalysts (Esso, Ger. Patent 1,028,266, 1958). Since the carbides are apparently very stable, similar behavior should be expected for carbon supported electrocatalysts.

Alloy catalysts have been of interest to workers in heterogeneous catalysis for some time. Much of the early work in this area was conducted with conventional metal alloys prepared in a form suitable for catalytic studies and it is now clear that alloying has a marked effect on the physiochemical properties of the constituent metals. A major theme of the work conducted has been the investigation of the relationship between catalytic activity and the electronic structure of metals (Schwab, Disc. Far. Soc., 8, 166, 1950 and Dowden and Reynolds, Disc. Far. Soc., 8, 184, 1950). The general approach for these studies is to correlate catalytic activity with alloy composition, the latter determining the electronic properties of the alloy. The alloys consisting of Group VIII and Group IB have received particular attention in this regard (Sinfelt, et al., J. Cat., 24, 283, 1972). The Group VIII metals have unfilled d-orbitals, while Group IB metals have a filled d-structure with an additional s-electron. By varying the alloy composition, the effect of d-orbital occupancy on catalytic activity could be observed. The d-electrons have been suggested frequently as playing an important role in the determination of catalytic properties.

The Engel-Brewer valence bond theory (Brewer, in Phase Stability in Metals and Alloys, P. Rudman, J. Stringer, and R. Jaffee, eds., McGraw-Hill, N.Y., 1967) has been remarkably successful in predicting the structure and stability of d-electron transition metals and alloys. The theory suggests that bonding between these elements occurs primarily through metal ligand bonds involving d-orbital overlap. More bonding orbitals are formed, hence a more stable structure is maintained due to donation of two paired electrons to the unfilled d-orbitals of zirconium. Changes in the d-orbital structure of platinum-transition metal compounds might be expected to produce dramatic changes in the catalytic properties of the constituent metals. It is this possibility which led Ross to investigate the Pt-Group IVB and Pt-Group VB intermetallic compounds for use as cathode electrocatalysts (Ross, Final Report EPRI EM 1553, 1980). Vulcan supported electrocatalysts were prepared by precipitating the base metal hydroxide onto a Prototech (Pt/Vulcan) catalyst. Subsequent heat treating to $> 900^\circ\text{C}$ resulted in stable intermetallic compounds having 30-50 Å crystallites. The vanadium, zirconium, and tantalum intermetallics all showed better cathode per-

formance than the Pt standard at 110°C. At 170°C only the vanadium intermetallic was superior. It was proposed that the intermetallic compound formation altered the heat of adsorption for oxygen, leading to a change in the rate of oxygen reduction. Preliminary stability testing indicated that those compounds having the Cu₃Au structure were the most stable. Both the vanadium and zirconium intermetallics were resistant to surface area loss under gas phase conditions suggesting long-term stability, even though surface area loss in liquid phase environments has been shown to be far different than for the same catalyst in the gas phase (Bett, et al., J. Cat., 35, 307, 1974 and Bett, et al., J. Cat., 41, 124, 1976). In later work (Ross, EPRI RP 1676-2, 1980), it was shown that the tantalum intermetallic was actually a two phase Pt₄Ta/Ta system. This catalyst exhibited better activity than the standard Prototech catalyst at 180°C. Furthermore, there was no appreciable change in the Pt cluster size after 1000 hr at 0.8V in 98% H₃PO₄ at 180°C. Palladium was also substituted for the platinum to form a series of Pd-Group IV and Pd-Group V intermetallic compounds. The Pd₃Nb intermetallic was of particular interest because it is isomorphic to Pt₃V. Reasonable dispersions for this catalyst could only be obtained for 5 w/o Pd loading, however, and the performance of these compounds was poorer than both Pt and Pt intermetallics.

The majority of performance testing of Pt intermetallics has been conducted below fuel cell operating conditions. Further testing of these materials is required at 180°C and above. It should be pointed out that the catalytic activity may be supplied only by the platinum. Previous work has been performed using Pt loadings identical to standard Pt/C electrocatalysts, and the kinetic parameters reported for the intermetallics are essentially the same as for platinum alone (Ross, EPRI EM 1553, 1980). Since all the transition elements form stable carbides, the rôle of the transition metal may be one of stabilizing the Pt crystallites.

3.5. Task 5 - Preparation of Platinum-Based Carbon-Supported Electrocatalysts

During this quarter electrocatalyst preparation focused on high surface area platinum tungsten and platinum molybdenum bimetallics supported on Consel I. These formulations were all prepared by an impregnation technique. The salt solutions were prepared to yield electrocatalysts containing 10 w/o Pt in the form of an alloy composed of 66 a/o Pt. Typically, about 1 g Consel I was added to the solution and the resulting slurry dried overnight at about 75°C. The dried catalyst was reduced in 10% H₂/N₂ at reduction conditions reported in Table I.

TABLE I

| <u>Catalyst</u> | <u>Reduction Condition</u> |
|-----------------|----------------------------|
| 14.7% Pt/W | 400°C for 2 hrs. |
| 12.6% Pt/Mo | 400°C for 2 hrs. |
| 14.7% Pt/W | 900°C for 1 hr. |
| 14.7% Pt/W | 900°C for 1 hr. |

The 400°C treatment was recommended by Kehl et al. (U.S. 3,639,647) for Ni/W or Ni/Mo catalysts to obtain superior alloy formulation and higher surface area.

The development of techniques for the preparation of platinum intermetallic catalysts was also initiated with the preparation of a platinum-vanadium intermetallic. This initial catalyst preparation consists of impregnation of a 10% platinum on Consel I catalyst with vanadium chloride, and heat treating the dried catalyst at 900°C in a 10% H₂/N₂ atmosphere. This heat treatment should both reduce the vanadium chloride to vanadium and facilitate alloying of the platinum and vanadium.

3.6. Task 6 - Characterization of Platinum-Based Carbon-Supported Electrocatalysts

Along with the preparation and testing of platinum sulphide catalysts as cathodes, some initial studies were made to find a method for determining the crystallite size. As shown in Figure 3 of last quarter's report (January-March 1981), the voltammogram for platinum sulphide is not significantly different from platinum.

If sulphur is present in the crystallite, which observation of the preparation procedure seems to indicate, it either does not have electrochemical activity which the cyclic voltammetry could detect, or sulphur is not present at the surface of the crystallite.

Determination of the crystallite size of supported platinum sulphide may possibly not be accomplished by either gas phase or electrochemical adsorption techniques. Thus far, no specific adsorbents which could be used for surface area determination of platinum sulphide have been found in the literature.

Qualitatively, the hydrogen adsorption charge of the voltammogram can be used as an indication of the surface area since the surface platinum present probably indicates the relative crystallite size. Pre- and post-test platinum surface areas are given in Table II for fine platinum sulphide preparations.

TABLE II

| <u>Catalyst No.</u> | <u>Surface Area (m²/g)</u> | | <u>% SA Lost</u> |
|---------------------|---------------------------------------|------------------|------------------|
| | <u>Pre-Test</u> | <u>Post-Test</u> | |
| EC-137 | 29 | 17 | 41 |
| EC-138 | 42 | 21 | 50 |
| EC-139 | 41 | 15 | 63 |
| EC-141 | 51 | 19 | 62 |

Interest in further characterization of this catalyst will be dependent on its performance as an oxygen reduction catalyst in phosphoric acid (see Task 7 below).

Initial attempts to characterize platinum-tungsten and platinum-molybdenum catalysts were made using cyclic voltammetry. There are no obvious features on the Pt/W voltammogram which show the presence of tungsten in the catalyst surface layer.

On the platinum-molybdenum voltammogram the hydrogen adsorption on platinum region of the curve is not as well defined, and an additional couple seems to appear at 500 mV (anodic) and 470 mV (cathodic).

Further investigation of the voltammetry of molybdenum and tungsten with platinum needs to be done in order to fully interpret these voltammograms. Measurement of the pseudocapacity under the hydrogen adsorption peaks, however, should give an indication of the surface area of platinum exposed and the crystallite size. These values for pre- and post-performance electrodes are tabulated in Table III.

TABLE III

| <u>Catalyst</u> | <u>Treatment</u> | <u>Pt Surface Area (m²/g Pt)</u> | |
|---------------------------|------------------|---|------------------|
| | | <u>Pre-Test</u> | <u>Post-Test</u> |
| 10% Pt + 4.7% W/Consel I | 400°C - 2 Hrs. | 16 | 16 |
| 10% Pt + 2.6% Mo/Consel I | 400°C - 2 Hrs. | 23 | 14 |
| 10% Pt + 4.7% W/Consel I | 900°C - 1 Hr. | 30 | 13 |
| 10% Pt + 2.6% Mo/Consel I | 900°C - 1 Hr. | 31 | 31 |
| 9.9% Pt + 0.9% V/Consel I | 900°C - 1 Hr. | 77 | 44 |

If this measurement is any indication of the crystallite size, then these catalysts do not have high surface areas and are not expected to perform well as cathodes in phosphoric acid. The apparent increase in the surface area from 400°C heat treat to the 900°C heat treat is probably due to a surface rearrangement of the platinum-tungsten and platinum-molybdenum atoms, with subsequent exposure of more platinum atoms. Obviously, additional surface characterization techniques need to be pursued before the surfaces of these catalyst crystallites can be fully understood.

The voltammogram of supported platinum-vanadium electrocatalysts was obtained. Additional peaks have appeared at high potentials (700-1100 mV) but little if any effect is seen at the lower potentials. Again, further investigation needs to be done to fully understand what information the voltammogram contains but surface area information can be derived from it. The pre-performance test surface area of the platinum-vanadium catalyst is 77 m²/g Pt, and the post-test surface area is 44 m²/g Pt. These areas are lower than the surface area of the platinum on Consel I precursor used to make this catalyst which was 110 m²/g Pt. Addition of vanadium has decreased the platinum surface area from 110 m²/g to 77 m²/g. This surface area loss may be due to the severe heat treatment (900°C) needed to react the platinum with vanadium.

3.7. Task 7 - Catalytic Activity of Platinum-Based Carbon-Supported Electrolytes

The best performance obtained thus far on a platinum sulphide catalyst is shown in Figure 1. This figure should be compared to Figure 2 which is a performance plot of a baseline 10% Pt on Vulcan XC-72R catalyst. The activity of the platinum sulphide catalyst at 900 mV is 7.2 mA/mg PtS₂ versus 24 mA/mg for platinum. This is not surprising since the surface area of the platinum sulphide is probably very low (see Task 6 above). The Tafel slope for platinum sulphide is 120-130 mV/decade whereas the platinum on Vulcan XC-72R has a Tafel slope of 110 mV/decade. Since the Tafel slopes are similar, granted that perhaps the structure of the platinum sulphide catalyst electrode has not been optimized, it appears that the lower performance of the platinum sulphide catalyst may be due to the very low surface area obtained by present preparation techniques. There are significant gains yet to be made on improving the method of catalyst preparation.

As expected from the low surface areas measured for platinum-tungsten and platinum-molybdenum, the performances of these catalysts are lower than for platinum alone. The relevant performance data are given in Table IV with a comparison to a typical platinum on Consel I catalyst. The full performance curves for these catalysts are shown in Figures 3 and 4.

TABLE IV

| <u>Catalyst</u> | <u>Tafel Slope</u> | $\mu\text{A}/\text{cm}^2$ Pt at 900 mV <u>Activity (O_2)</u> | <u>Polarization (Air)</u> at 200 mA/ cm^2 |
|------------------|--------------------|--|---|
| Pt + W/Consel I | 120 mV/Decade | $69\mu\text{A}/\text{cm}^2$ | 555 mV |
| Pt + Mo/Consel I | 120 mV/Decade | $29\mu\text{A}/\text{cm}^2$ | 605 mV |
| Pt + V/Consel I | 120 mV/Decade | $90\mu\text{A}/\text{cm}^2$ | 700 mV |
| Pt/Consel I | 100 mV/Decade | $61\mu\text{A}/\text{cm}^2$ | 712 mV |

The data show that these catalysts do not perform as well as the best platinum on Consel I for oxygen reduction. This poorer performance could be due to the low surface area of these catalysts as presently prepared. Until a high surface area preparation of platinum with tungsten or molybdenum is developed, a valid determination of the performance of these catalysts cannot be made.

The performance of a platinum-vanadium intermetallic catalyst was determined and the performance curve is shown in Figure 5. The data are summarized in Table IV.

Even though the post-test surface area is only $44 \text{ m}^2/\text{gram}$, the performance of this catalyst is probably better than platinum alone. The activity of Pt-V for oxygen reduction is calculated to be $90\mu\text{A}/\text{cm}^2$, which is at the top of the range for platinum (L. Bregoli, *Electrochim. Acta*, 23, 489 (1978)). This high an activity for oxygen reduction is only occasionally measured for platinum on carbon catalysts. The polarization at 200 mA on air for Pt-V is 700 mV, which again is as good as for platinum on carbon. These results are very encouraging for Pt-V electrocatalysts. Optimization of the electrode structure and catalyst preparation will be pursued and should lead to the development of a superior oxygen reduction catalyst.

The companion EPRI 1200-2 program has developed advanced electrocatalyst supports, some of which have been utilized in this present DEN3-176 program. A new support, which is identified as Consel IV, has been developed in the EPRI 1200-2 program. This support has a graphitized carbon structure with an increased density of specific trap sites. The support was catalyzed using our process technology with the platinum-vanadium intermetallic. Performance data are shown for oxygen and air in Figure 6 (Electrode #99). Since we have not attempted to optimize electrode structures in this program, we have taken the liberty of identifying the

projected performance for this electrocatalyst and electrocatalyst support assuming an improved electrode structure. Reasonable performance parameters are a Tafel slope of 90 mV at 180°C, 100% phosphoric acid. We have, therefore, assumed that the lower Tafel performance exhibited in Figure 6 is due solely to a non-optimized electrode structure. Given these assumptions, the performance data would be shown as the solid lines in Figure 6 and tabulated in Table V.

It should be noted that within reasonable experimental assumptions that the performance for pure oxygen at atmospheric pressure is equivalent to the performance in pressurized fuel cells for air at 5 atm. To the best of our knowledge, these performance levels, shown in Figure 6, have not previously been seen for any other electrocatalyst and support system.

In order to further characterize this electrocatalyst and electrocatalyst support, anode performance data were obtained and are shown in Figure 7. Although the performances under 10% carbon monoxide and 30% carbon monoxide are reasonable, they do not yet match those performances we have previously seen for diffusion-free electrode structures and, therefore, further gains in the electrode performance with electrode structure improvement are to be expected. Moreover, there will be an additional gain with improvements in the catalyzation techniques to achieve higher surface area metal electrocatalyst particles.

TABLE V

Electrode P99 - 0.5 mg Pt/cm² Electrode

| <u>$\frac{i}{\text{mA/cm}^2}$</u> | <u>Air at Atmospheric</u> | | <u>Pure O₂ at Atmospheric and Air at 5 atm.</u> | |
|--|---------------------------|-----------------------------|--|-----------------------------|
| | <u>Actual</u> | <u>Projected</u> | <u>Actual</u> | <u>Projected</u> |
| 300 | 686 | 725 (mV vs H ₂) | 757 | 805 (mV vs H ₂) |
| 200 | 714 | 750 | 781 | 820 |
| 100 | 755 | 775 | 819 | 850 |
| 10 | 865 | 870 | 939 | 940 |

3.10. Task 10 - Survey of Aging

Recent advances in hydrocarbon fuel processing have widened the range of fuels from which hydrogen can be obtained (Catalytica Associates, EPRI EM 570, 1977 and Arthur D. Little, Inc., EPRI EM 695, 1978). The variety of impurities, therefore, has also expanded. How the fuel cell responds to impurities determines the level of sophistication required for fuel clean-up and construction of cell components. During this quarter, effects of poisons and impurities on fuel cell performance are reported. The literature on long-term impurity effects is sparse with the exception of the effects of those contained in the fuel or produced during fuel processing. Based on the work conducted to date, Table VI shows the impurity levels that can be tolerated in phosphoric acid fuel cells without suffering significant performance decline (KTI Corp., EPRI EM 1487, 1980 and Benjamin et al., DOE EC-77-C-03-1545, 1980).

Hydrocarbon impurities are produced in the steam reforming process and are of importance at the anode. Naphtha, No. 2 fuel oil, and now possibly heavy liquid fuels derived from coal and shale oil are used for the manufacture of hydrogen fuel. Concurrent with the steam reforming reactions are the water-gas shift and methanation reactions. Also, natural gas feedstocks will contain small amounts of unreacted methane, or methane formed from the higher hydrocarbons which make up natural gas. Traces of C_2 and higher hydrocarbons may also be present for the liquid fuels, since both steam cracking and catalytic cracking may occur (Schnell, J. Chem. Soc. (B), 158, 1970). Long term testing of these impurities has been reported for methane only (UTC, EPRI EM 335, 1976). Fuel cells were subjected to feed streams containing up to 15% methane for periods of up to 5,000 hours duration. The only effect was apparently a diluent effect, the drop in performance attributed to lower hydrogen composition. The anode electrocatalysts were analyzed by electron microscopy and cyclic voltammetry, and the electrolyte was chemically analyzed at the conclusion of the test. These analyses confirmed that methane was both chemically and electrochemically inert. The longer chain hydrocarbons exhibit poisoning effects at the anode (Benjamin, DOE 1545, 1980). This is probably due to chemisorption by C-C bonds on multiple platinum sites. Any reactions of these adsorbed entities will be slow, hence the catalyst will show an apparent decrease in activity. There have been no reported in-depth studies concerning the long term effects of C_2 and higher hydrocarbon compounds on fuel cell performance. Up to now, steam reforming technology for naphthas and other light and middle distillate fuels is available to produce fuel cell feeds containing only trace quantities of these species. Nevertheless, future use of liquids derived from shale or residuum oils could increase the impact

of these hydrocarbons on long term fuel cell performance. Advances in steam reforming may be required to keep the hydrocarbon level below 100 ppm.

Other carbon based impurities will be present in anode feeds, namely CO and CO₂. Like the hydrocarbon impurities, these gases are also produced during reforming. Shift converters remove carbon monoxide which seriously diminishes the performances of anode electrocatalysts. Carbon dioxide, on the other hand acts only as a diluent. Anode poisoning by carbon monoxide occurs by site elimination (Kohlmayer and Stonehart, *Electrochimica Acta*, 18, 211, 1973). The apparent Pt activity is decreased and anode polarization is increased substantially. Recent developments in fuel cell materials have resulted in an increase of operating temperature to the 180-200°C range. The threshold limit reported in Table VI is for 160°C. Since CO poisoning is dependent on temperature (see Figure 8), this change of operating conditions to higher temperatures will allow tolerance of higher CO feed concentrations. Novel alloy electrocatalysts have been shown to be superior to platinum for up to 30% CO anode feeds at 180°C (Stonehart Associates, Inc. DOE-0176, 1981), and further increases in temperature may eliminate CO from consideration as an impurity problem. The long term effects of CO poisoning are reversible when the carbon monoxide is removed from the feed (UTC EPRI EM 576, 1977). Synergistic effects of carbon monoxide and other impurities are discussed later.

Nitrogen compounds enter the fuel cell with both fuel and oxidant streams. Air is used as the oxidant so nitrogen gas is present in large quantities at the cathode. The nitrogen acts only as a diluent; no long term deleterious effects have been observed. The diluent effect of nitrogen gas is also observed at the anode. Here, nitrogen is generally introduced by nitrogen containing hydrocarbons. Compounds such as NH₃, HCN, and NO_x, however, may also be formed. These nitrogen containing compounds may still be produced even if nitrogen-free feedstocks are used if the fuel processing scheme includes autothermal reforming or coal gasification (Catalytica Associates, Inc., EPRI EM 570, 1977). All of these nitrogen compounds result in decreased fuel cell performance. The available literature deals largely with the problems associated with the introduction of ammonia.

Ammonia reacts with phosphoric acid to form ammonium dihydrogen phosphate. Very low levels of ammonia can be tolerated in the fuel cell without noticeable performance loss (United Technologies, Inc., EPRI EM 335, 1976). If the phosphoric acid is ammoniated to greater than 0.2 mole %, significant performance loss is observed (Szymanski, et al., *Electro. Chem. Soc. Meet.*, Pitt., 1978). Various

theories have been advanced to explain the performance decrease (Benjamin, et al., DOE EC 77-C-03-1545, 1980), among them poisoning of the platinum at the cathode and decrease of the conductivity of the acid. In the work of Szymanski, et al., an 84% loss of "cathode activity" was reported for 1% conversion of acid to ADHP. This was believed to occur because of oxidation of ammonium ion at the cathode. A conductivity decrease theory, however, would also account for this performance decrease. For oxygen reduction to occur, hydrogen ion must migrate from the anode to the cathode. Regardless of the mode of transfer (diffusion of H^+ or proton chain conduction, for example), a decrease in solution conductivity lowers the H^+ concentration at the cathode resulting in a concomitant decrease in performance. Long term performance testing has been conducted to determine the effects of sustained introduction of ammonia. Constant levels of ADHP were reached, but these concentrations were much lower than would be predicted on the basis of complete conversion of inlet ammonia concentrations. This result, coupled with the fact that performance can be restored on removal of ammonia from the feed (see Figure 9), leads to the conclusion that the ammonium ion can be oxidized at the cell operating conditions.

Advanced fuel processors operating on petroleum or coal derived liquid fuels produce H_2S . An adiabatic reformer using No. 2 fuel oil, for example, is expected to produce an anode fuel containing about 320 ppm H_2S (UTC, EPRI EM 1328, 1980). This gaseous sulphur compound must be removed before the fuel reaches the cell stack. Sulphur compounds severely poison platinum based electro-catalysts. The introduction of 130 ppm H_2S to cells operating at $205^{\circ}C$ caused rapid performance decay (UTC, EPRI EM 576, 1977) after a short period of stable operation. Similar behavior was observed for 180 ppm H_2S at $190^{\circ}C$ (UTC, EPRI EM 956, 1978). Stable operation was observed for about 400 hr in this test before performance decayed rapidly. In general, operation of fuel cells on fuels containing ppm quantities of H_2S are characterized by periods of stable operation followed by rapid performance decreases (Benjamin, DOE EC-77-C-03-1545, 1980). Original performance can be restored by removing H_2S from the feed as shown in Figure 10. As with carbon monoxide, the poisoning apparently occurs by site elimination. Improved tolerance to sulphur compounds has been reported for temperatures in excess of $200^{\circ}C$ (UTC, EPRI EM 956, 1978).

Operation of cell stacks on fuels containing both CO and H_2S has also been examined (UTC, EPRI EM 576, 1977). Rapid decay is observed following introduction of these poisons to the cell stack. Original performance can be approached

or restored completely by removing either CO or H₂S or both. This provides strong evidence for a synergistic effect between these poisons. Thermodynamic calculations indicate that about 0.5 ppm carbonyl sulphide would be in equilibrium with a simulated reformer effluent containing 200 ppm H₂S. It is conceivable, therefore, that COS is formed on the anode by reaction between CO and H₂S. Several tests have been run with 1 ppm COS added to the fuel, but no observable performance loss attributable to COS was observed in the temperature range 175-200°C (UTC, EPRI EM 956, 1978). It is clear from this observation that H₂S-CO interaction with the electrocatalyst is complex and, at this time, far from being understood.

Electrodes exposed to sulphur concentrations for long time periods have been examined to identify any structural changes which could be attributed to the sulphur alone. No observable changes in the electrodes could be detected and no changes in catalyst properties were found (UTC, EPRI EM 576, 1977).

Poisoning of electrocatalysts by metals may also occur. The steam reforming and shift conversion catalysts are subject to physical degradation. It would be expected, therefore, that trace quantities of metals such as nickel, copper, and zinc might be introduced in the fuel stream. Vanadium is known to be present in middle and heavy distillate fuel and may cause serious problems if residuum fuels are used (Gates, Katzer, and Schuit, "Chemistry of Catalytic Processes," McGraw Hill, N.Y. 1979). Iron and copper metals can be leached from hardware if protective coatings are etched. Large polarization (above 50 mV) has been attributed to copper poisoning (UTC, DOE FCR 1303, 1979). Finally, iron is also present in carbon and can be leached, for example, from the graphite end plates.

4. Changes

There are no changes in the program.

5. Problem Areas

There are no problem areas at this time.

Addendum

Figures 1 through 7 of this report show our computer generated plots for electrode performance data. The current density axis is dimensioned as log mA/cm² electrode. The electrode potential is dimensioned in mV vs RHE. The printout format has an option to include or exclude the grid. In addition, a rapid comparison is provided for any electrode performances that are stored in memory by simply calling the electrode numbers and plotting the data sets into the same figure. This computer generated format will now be used for our reports.

TABLE VI

Maximum Allowable Impurity Levels for
Phosphoric Acid Fuel Cells

| <u>Impurity</u> | <u>Limit</u> |
|---------------------------|-----------------|
| Hydrocarbons | |
| CH ₄ | dil. |
| C ₂ and higher | 100 ppm |
| Carbon | |
| CO | 4% ¹ |
| CO ₂ | dil. |
| Nitrogen | |
| N ₂ | dil. |
| NH ₃ | .1-1 ppm |
| Sulphur | |
| COS | 100 ppm |
| H ₂ S | 100-200 ppm |
| Metals | |
| Fe | trace |
| V | trace |
| Cu | trace |
| Others | |
| Cl ⁻ | 1 ppm |
| H ₂ O | dil. |

¹ CO tolerance is a function of temperature so operating conditions will determine maximum allowable concentration.

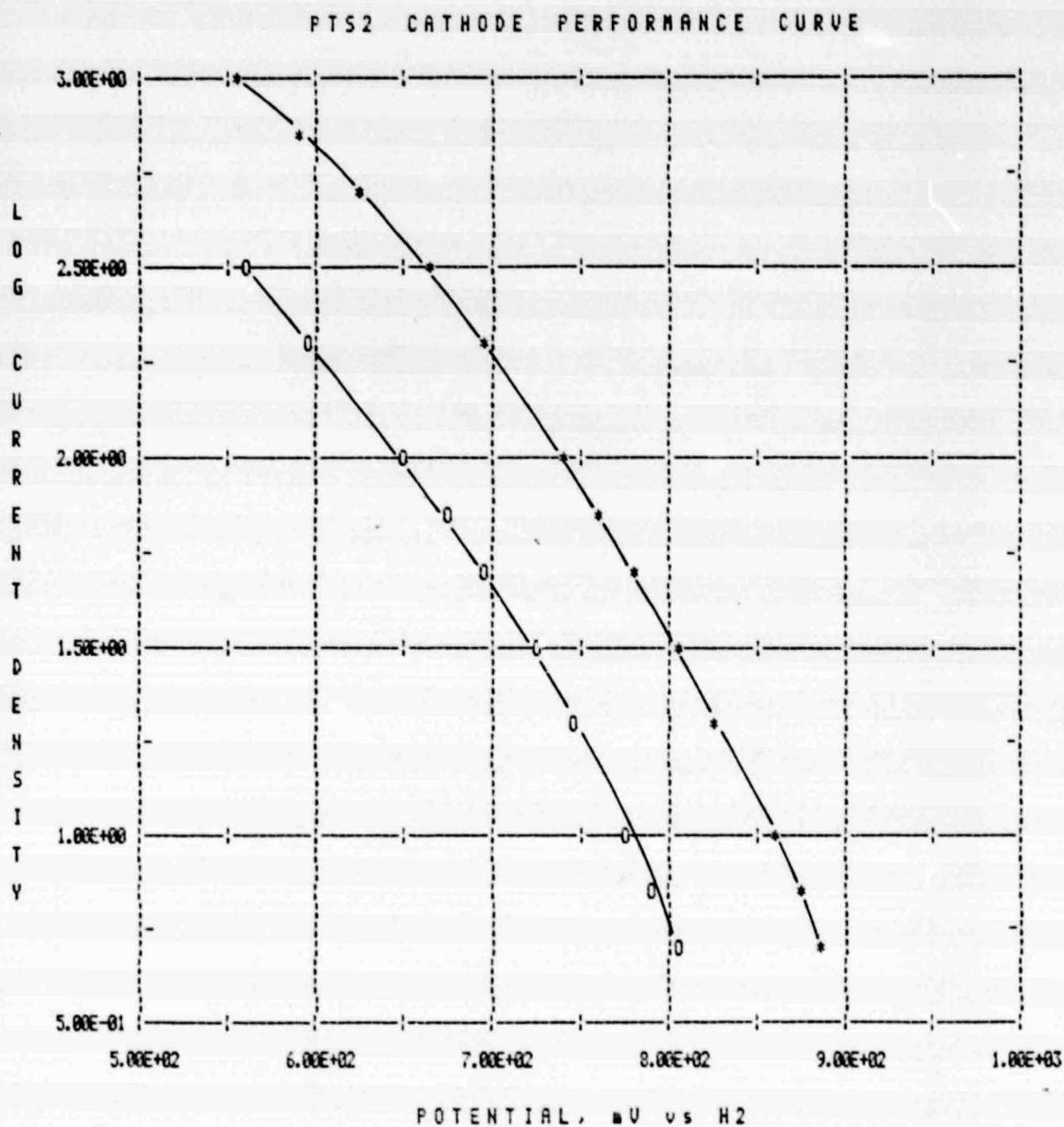


FIGURE 1.

Cathode performance of a 10% PtS₂/Consel I catalyst in 180°C, 100% H₃PO₄ on air(O) and O₂(*). Electrode loading = 0.5 mg PtS₂/cm².

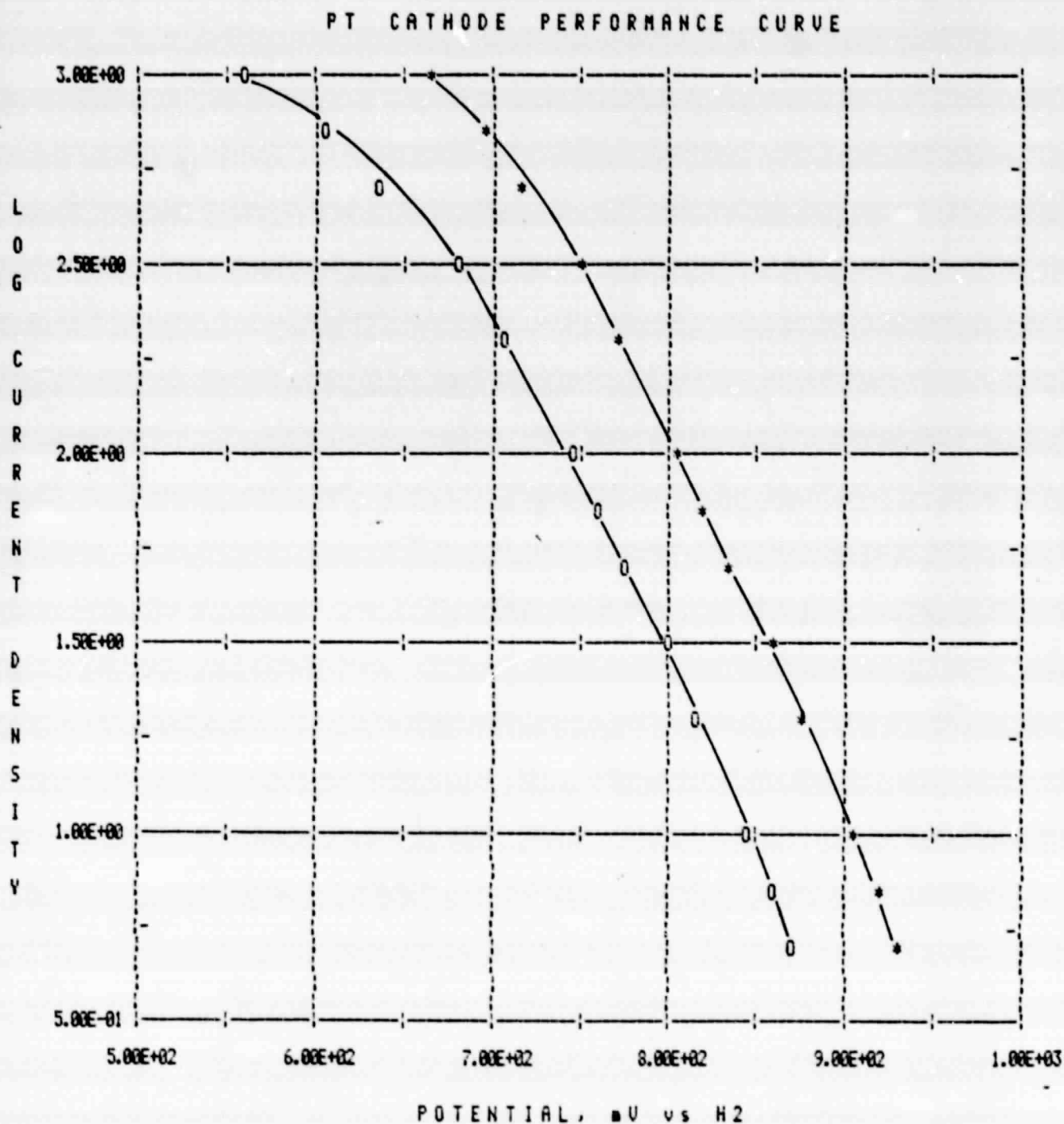


FIGURE 2.

Cathode performance of a 10% Pt/Consel I catalyst in 180°C, 100% H₃PO₄ on air(0) and O₂(*). Electrode loading = 0.5 mg Pt/cm².

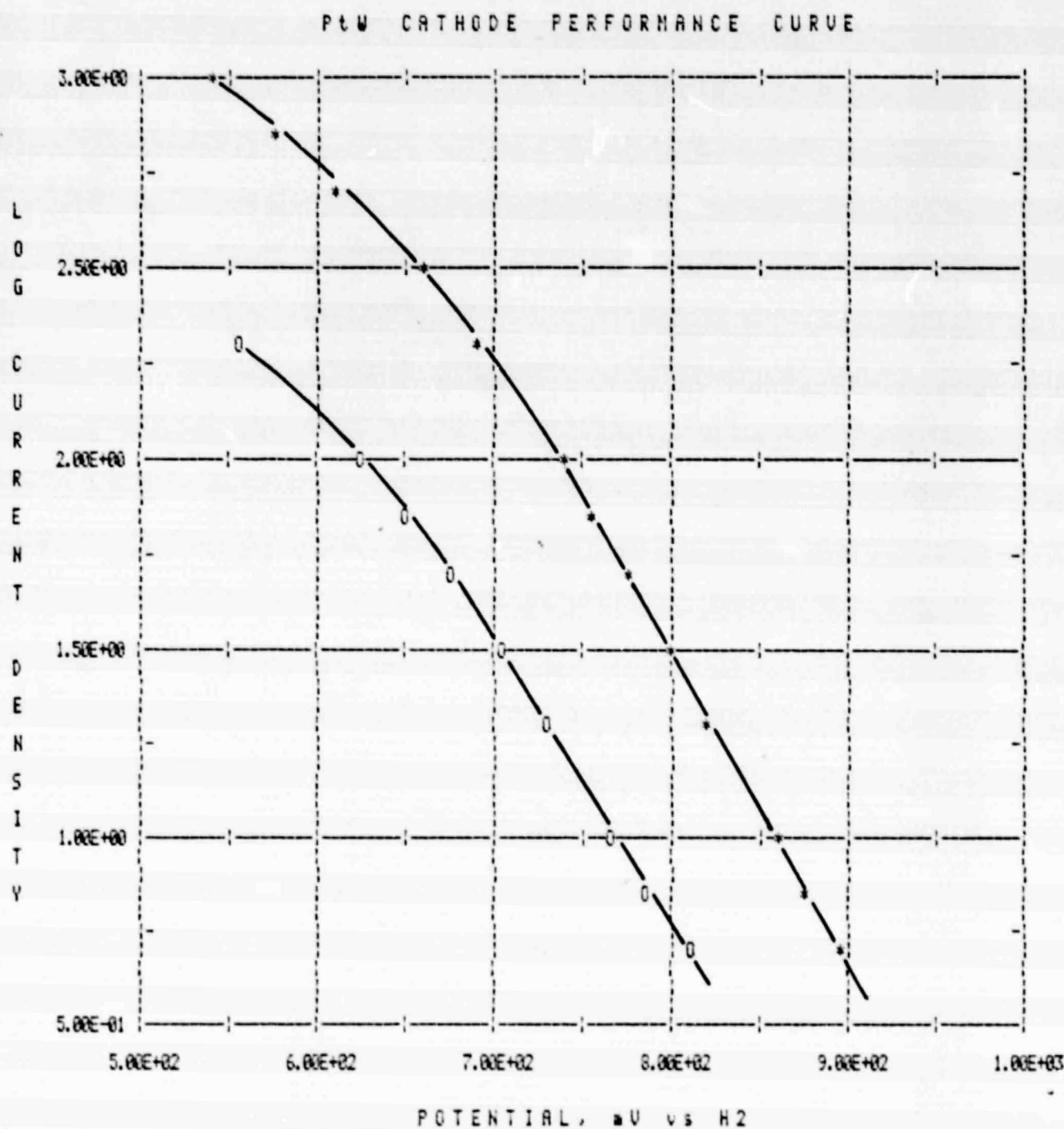


Figure 3.

Cathode performance of a Pt-W/Consel I catalyst in 180°C, 100% H₃PO₄ on air (0) and O₂ (*). Electrode catalyst loading = 0.73mg Pt-W/cm². 68%Pt/32%W.

PLMo97 CATHODE PERFORMANCE CURVE

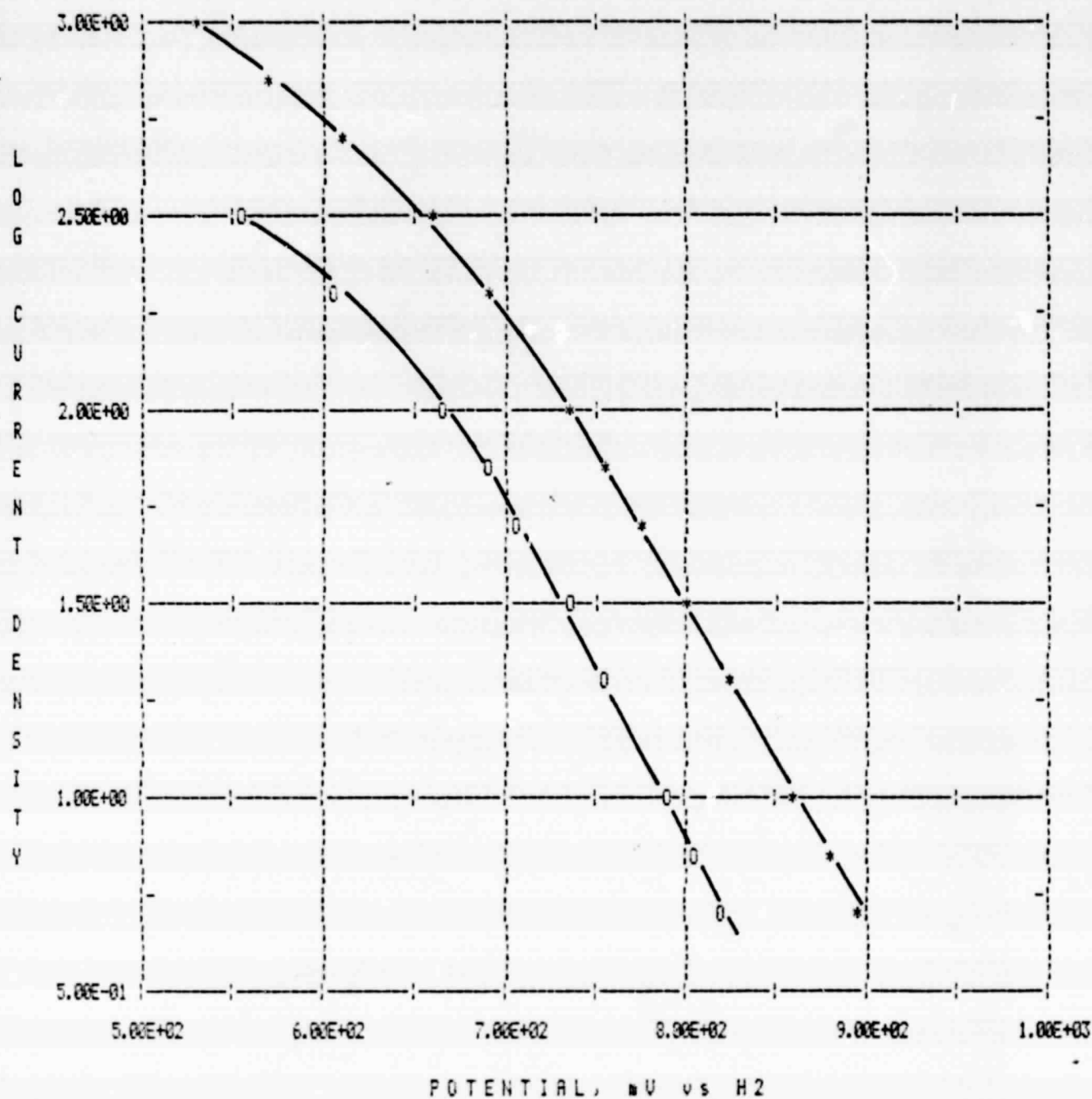


Figure 4.

Cathode performance of a Pt-Mo/Consel I catalyst₂ in 180°C, 100% H₃PO₄ on air(0) and O₂(*). Electrocatalyst loading = 0.63Pt-Mo/cm². 79%Pt/21%Mo.

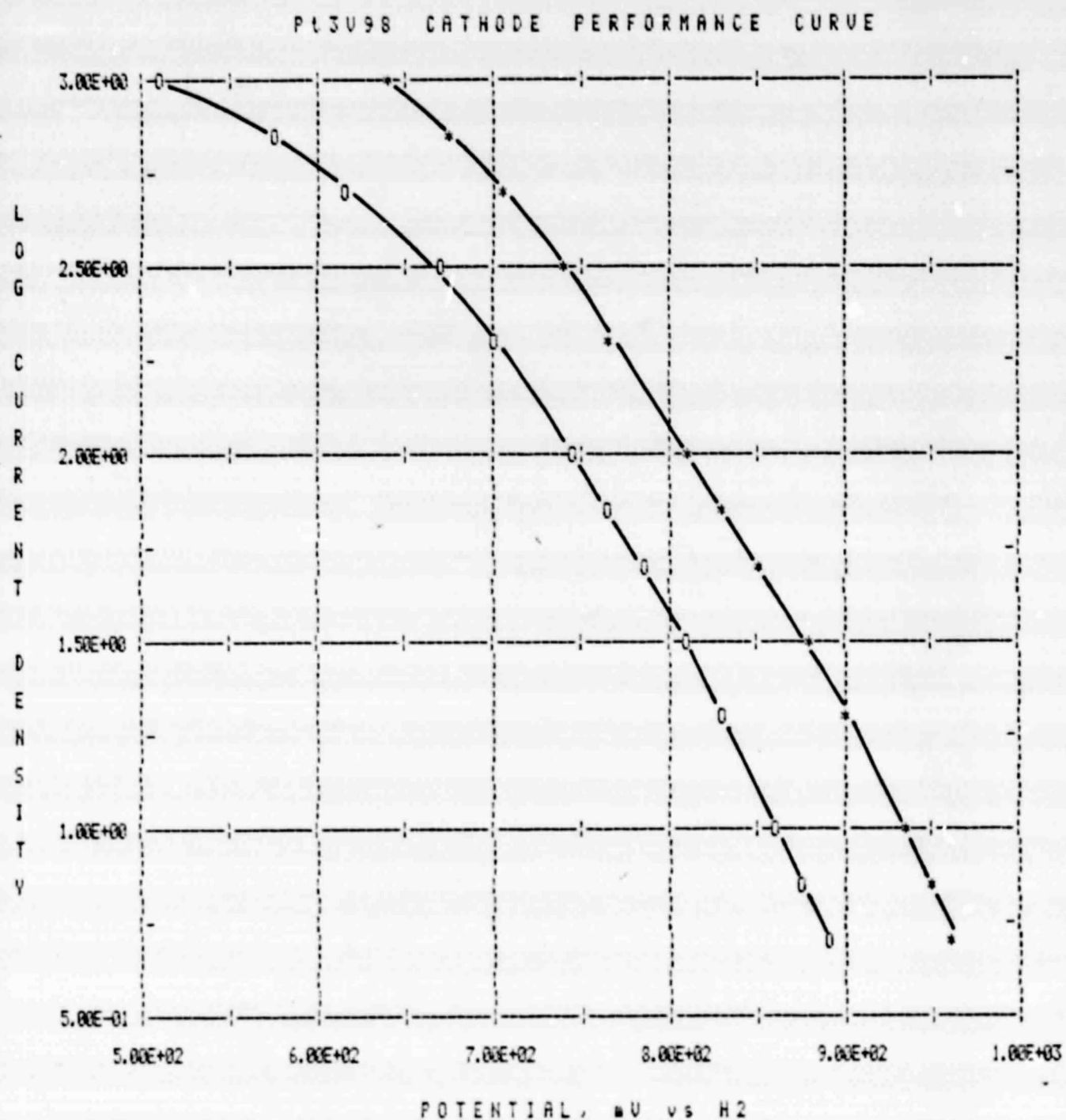


Figure 5.

Cathode performance of a Pt₃V/Consel I catalyst in 180°C, 100% H₃PO₄ on air(0) and O₂(*). Electrode loading 0.54mgPt₃V/cm². 92%Pt/8%V.

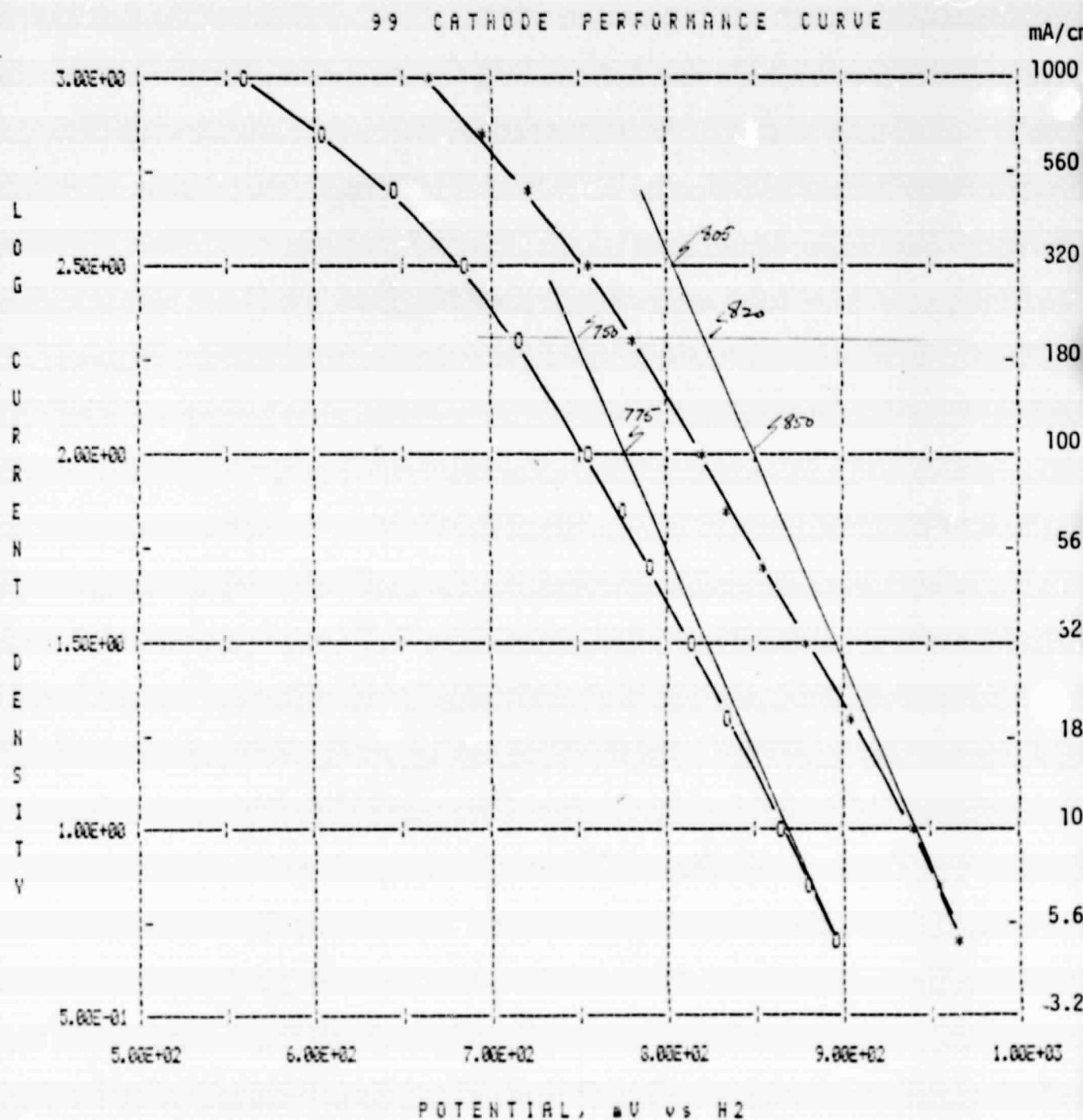


Figure 6.

Electrode P99 cathode performance for a Pt₃V Consel IV catalyst .5 mg Pt/cm² electrode. 180°C, 100% H₃PO₄ on air (O) and O₂ (*).

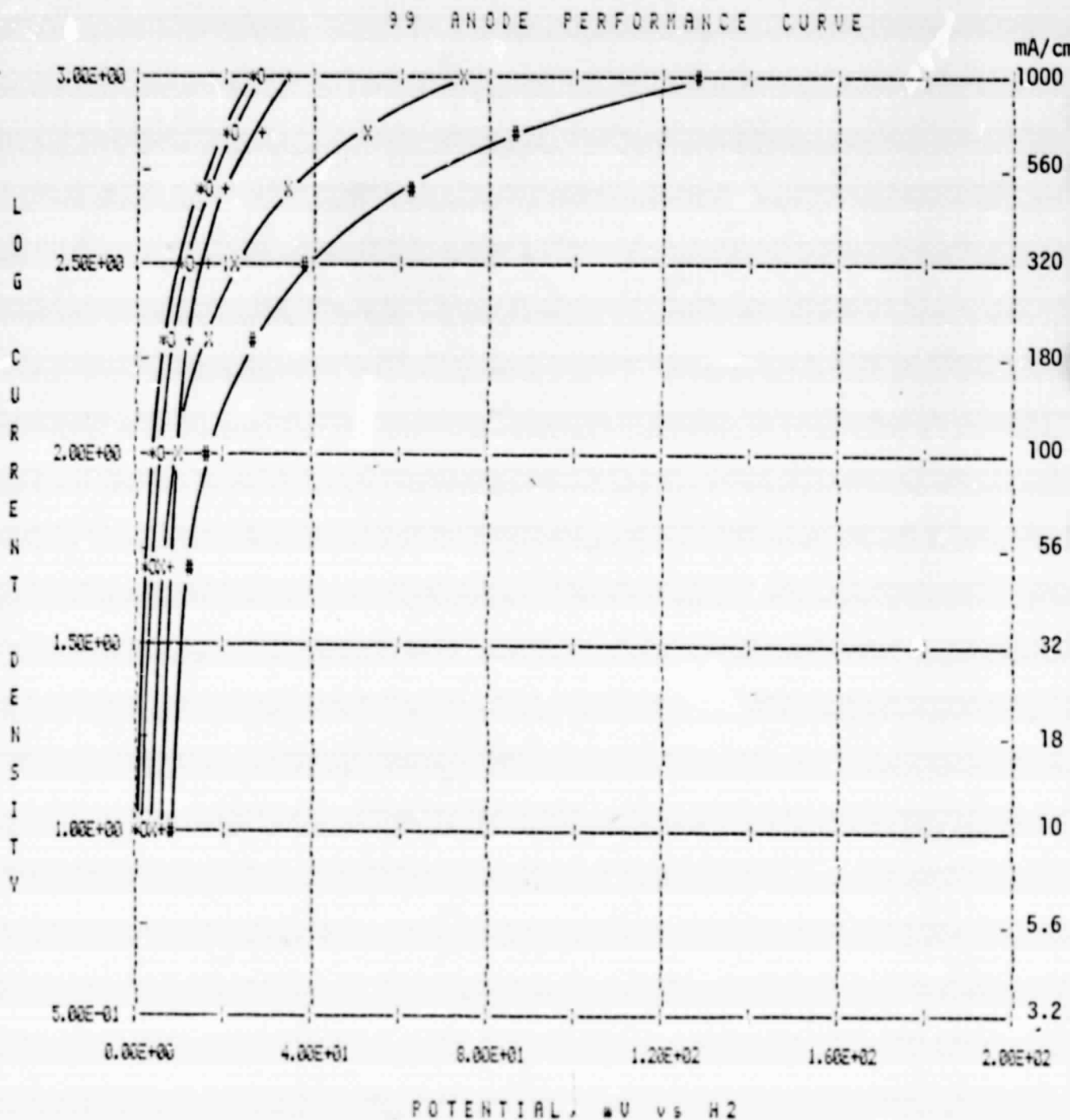


Figure 7.

Anode performance curves on electrode P99 (see Figure 6), 180°C, 100% H₃PO₄.
 100% H₂ (*), 90% H₂ 10% N₂ (O), 70% H₂ 30% N₂ (+), 90% H₂ 10% CO (X), 70% H₂
 30% CO (#).

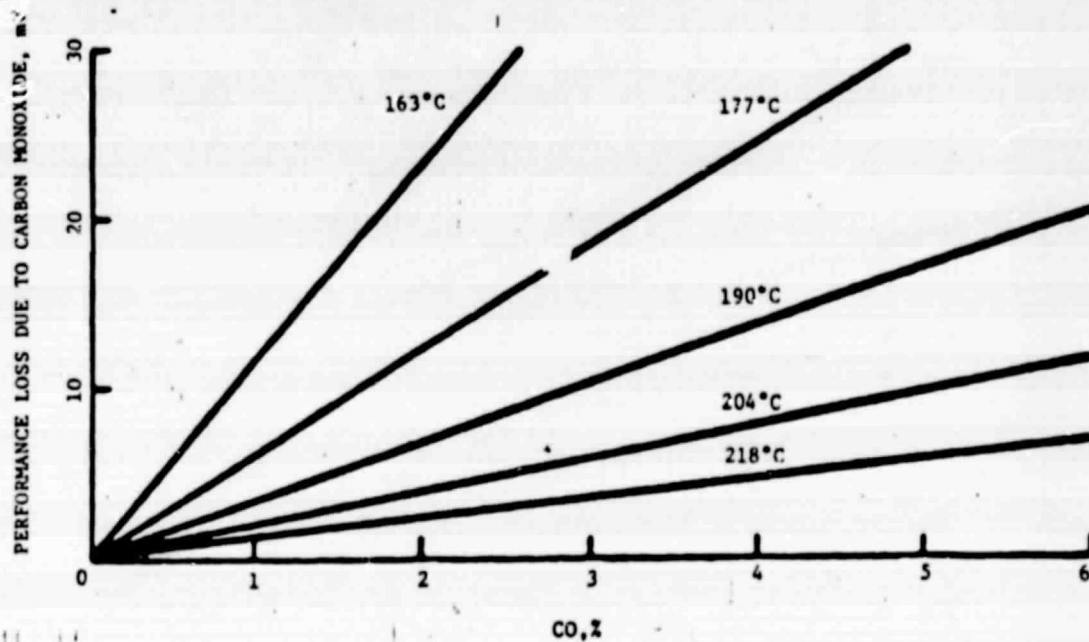


Figure 8.

Effect of CO content and temperature on anode performance. 0.35 mg Pt/cm^2 , 269 mA/cm^2 .

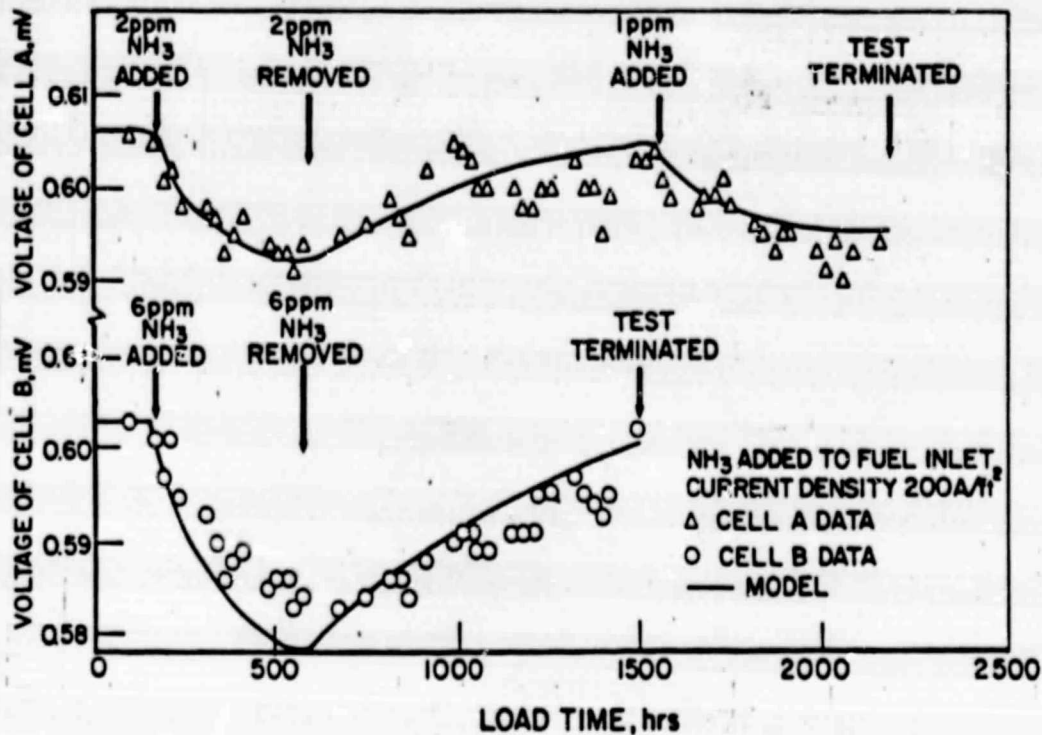


Figure 9.

Cell endurance in the presence of ammonia

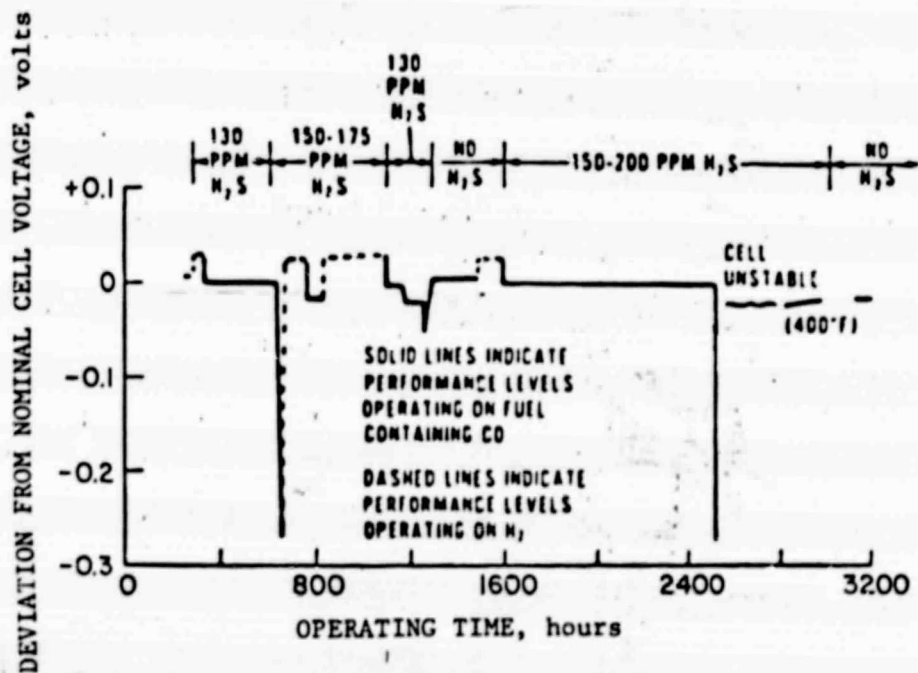


Figure 10.

Effect of H₂S on phosphoric acid fuel cell performance.